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Release coatings for pressure sensitive adhesives

DAVID J. KINNING* and HILDEGARD M. SCHNEIDER

3M Company, St. Paul, MN, USA

1. Introduction

Release coatings are important components of pressure sensitive adhesive (PSA) products such as tapes and labels [1]. Release materials are coated onto the backside of PSA tape backings (often called low adhesion backsizes or LABs in this form) to provide the desired tape roll unwind force. They are also coated onto various substrates to form release liners for PSA products such as labels and transfer tapes. Typically the thickness of the release coating is less than 1 μm , and often times less than 0.1 μm . Release coatings can be thought of as the PSA delivery system, providing a controlled unwind or release force and protecting the adhesive from contamination and unintentional contact until it is applied.

The requirements for a release coating include:

- (1) Providing a release force desired for the intended application. The release forces provided by a release coating are often categorized as premium, between about 1 and 10 g/cm, modified, between about 10 and 50 g/cm, or tight, between about 50 and 500 g/cm. Release materials for liners are generally formulated to provide premium to modified release, while release materials for low adhesion backsizes are usually in the tight range.
- (2) The release force must be stable under whatever environmental (e.g., temperature and humidity) conditions the PSA product will experience.
- (3) The release material should be well anchored to the backing so that it does not transfer to the PSA, thereby decreasing the subsequent PSA adhesion (herein referred to as readhesion). Similarly, the release material should not contain labile components that could transfer to the PSA and decrease the readhesion by an unacceptable amount.

Some additional requirements of the release coating may include the ability to write, print, or paint onto it, to provide quiet or smooth unwind, or to exhibit low coefficient of friction. There is also a trend towards the use of solventless release materials in the form of waterbased or 100% solids coatings.

The types of polymers that are used as release coatings include silicone networks, silicone containing copolymers, polymers with long alkyl or fluoralkyl side chains, fluoropolymers, and polyolefins. These polymers have surface energies that are less than the surface energies of commonly used PSAs, an important feature of release materials.

2. Release mechanisms

2.1. Surface energy and work of adhesion

The release of a pressure sensitive adhesive from a release coating is a complex phenomenon [1]. Many factors can play a role in determining the force necessary to peel a PSA from a release coating other than just the choice of the release material, including the PSA rheology, PSA chemical composition, PSA surface energy, potential chemical interactions at the PSA/release coating interface, the rheology and topology of the backing, the processing conditions used to coat or cure the release material, and the testing conditions. In this chapter, the effect of the release material chemistry, surface and interfacial composition, and rheology on release performance will be emphasized, in addition to the potential chemical interactions between the PSA and release coating. Consider the situation of a PSA tape being peeled from a release coated substrate. According to the conventional theories of adhesion [2,3], the work required to peel the tape can be written in the form

$$\text{Work to peel} = W_a \times f(v, T)$$

where W_a is the thermodynamic work of adhesion, determined by the strength of the chemical interactions at the PSA/release coating interface, and is given by the equation

$$W_a = \gamma_a + \gamma_r - \gamma_{ar}$$

Where γ_a is the surface energy of the adhesive, γ_r is the surface energy of the release coating, and γ_{ar} is the interfacial energy between the adhesive and release coating. $f(v, T)$ is a function which describes the energy dissipated during the peeling, for example in the form of irreversible deformation of the PSA, release coating, or backing. The amount of energy dissipation, and thus the peel force, will depend on the peeling rate, v , and temperature, T . As the PSA is peeled from the release coating the PSA will deform, and the deformation will have both an

Table I

Surface energies of the chemical constituents commonly found in PSA release coatings

| Constituent | Surface energy, γ (mJ/m ²) |
|---------------------------------------|--------------------------------------------------|
| Hydrocarbon segments | |
| -CH ₃ | 23.0 |
| -CH ₂ - | 35.9 |
| Fluorocarbon segments | |
| -CF ₃ | 14.5 |
| -CF ₂ - | 22.6 |
| Polydimethylsiloxane | |
| -Si(CH ₃) ₂ O- | 19.8 |

Several authors have examined the effect of substrate surface energy on the tack or peel force of pressure sensitive adhesives. For example, Dahlquist [14,15] found that the peel forces for a rubber-resin type PSA peeled from various polymer substrates generally increased with increasing surface energy of the substrate, although there was considerable scatter in the data. Toyama and coworkers [10,11] measured the tack and peel force of rubber-resin and acrylate based PSAs for polymer surfaces having critical surface tensions between 18 and 43 mJ/m². They found that, for substrate surface tensions less than that of the PSAs (35–36 mJ/m²), both the peel and tack force increased with increasing substrate surface tension. At higher substrate surface tensions a decrease in the peel and tack force was seen. In contrast, Sherriff et al. [12] observed a monotonic increase in the tack of rubber-resin PSAs as the probe surface energy was increased from 18 to 42 mJ/m². Zosel [13] found that the adhesive failure energy of polyisobutylene PSAs, peeled from substrates with surface tensions between 19 and 44 mJ/m², increased with increasing substrate surface tension until the substrate surface tension reached that of the PSA. At higher substrate surface tensions the adhesive failure energy remained fairly constant. The common finding in these studies is that the PSA adhesion generally decreases at the lower substrate surface energy, consistent with the thought that a release material needs to have low surface energy. However several authors have pointed out that there is often a lack of correlation between the magnitude of the PSA release force and the release material surface energy [7,16–19]. While a low surface energy is a prerequisite for a polymer to be a good PSA release material, it alone does not guarantee good performance under all aging conditions [19,20]. The surface energy of the release coating is an important contributing factor in determining the release force of a PSA, but it is clear that other phenomena can also play important roles.

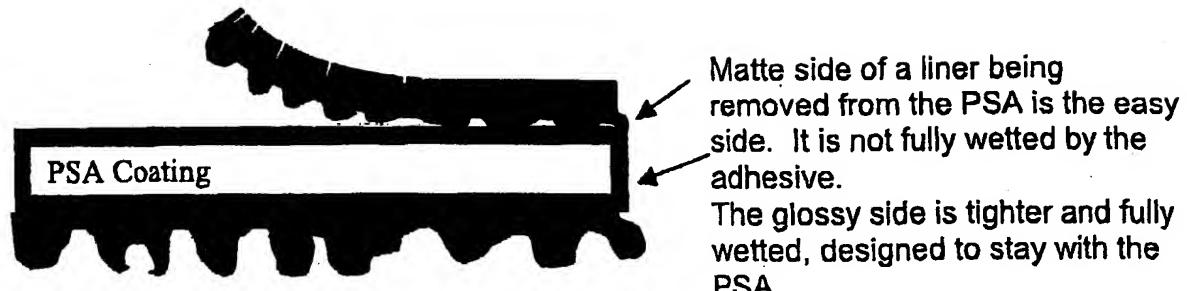


Fig. 1. PSA coating example.

2.2. Topological considerations

When considering release mechanisms, the physical and chemical heterogeneity of the adhesive/release interface cannot be ignored. At its most basic level, roughness of the release and PSA surface, the stiffness of the PSA and the method in which the PSA and release surface are brought together define the contact area of the interface. The area of contact between the PSA and release material defines not only the area over which chemical interactions are possible, but also potential mechanical obstacles to release. In practice, a differential liner for a transfer adhesive can be made to depend in part on the substrate roughness for the differences in release properties [21].

In the example illustrated in Fig. 1, the PSA is coated from solution onto the glossy side of the liner, which is the tight release side. After drying the adhesive solution, the PSA and liner are wound into a roll and in winding the rough matte side is brought into contact with the adhesive. Since the PSA was solution coated onto the smooth side of the liner, the more intimate contact offers slightly higher release force than the matte side of the liner, which is just wound in place. The roughness scale of the matte patterning and the stiffness of the PSA are sufficient to avoid PSA penetration even when being aged in roll form. One must, however, also recognize that (with different coating methods or PSA stiffness) the opposite is possible and that penetration of PSA into micro or macrostructured liners will increase contact, possibly increasing surface interactions as well as mechanical energy dissipation during peel. Finally, a patterned release coating may make an impression on the PSA that can alter its subsequent adhesion. This property can be beneficial or detrimental to the PSA performance, and should be carefully controlled. Utilization of substrate roughness is one route to modifying release properties, but is not commonly used without also modifying the surface with particular release chemistries.

2.3. Chemical patterning

Heterogeneity extends beyond the geometric, and chemical patterning can also be critical. Chemically patterned release surfaces can result in various levels of

regularity, from microphase separating blends of release polymers [22], unintentional artifacts of coating [23], intentionally pattern coated release systems [24], or subsequent purposeful 'damage' of release coatings [25,26]. Typically, the size scale of microphase separation is small enough that the system presents a uniform release level over measurable length scales which is an average of the composition of the release systems employed. One must realize that surface energetics will influence the composition presented to the PSA relative to that in the bulk, and that subsequent restructuring is possible. Phase separation is most commonly used in silicone acrylates or epoxysilicones when blending polymers of varying levels of functionality. Manipulating release values by intentionally damaging certain parts of a release surface, like those partially exposed to corona, can produce differential release levels. Intentionally pattern coated surfaces employing either differential chemistries or differential coat weights have measurable variation in release comparable to the length scale of the pattern, however if the system is appropriately chosen, the desired peel level and character can be controlled and maintained [24].

2.4. Interdiffusion

Another important adhesion mechanism between polymers is that of interdiffusion. However, most pairs of high polymers are incompatible, and a narrow interface (interphase) is expected to form between them. Since most release coatings have a significantly lower surface energy than that of the PSAs, they will have a high degree of incompatibility with the PSA, and interdiffusion would not be expected to contribute significantly to the adhesion level. An exception to this generality is the specific combination of silicone release coatings and silicone PSAs. Unless the silicone release coating is highly crosslinked [27], interdiffusion can occur leading to increasing release forces with time. Usually silicone PSAs require the use of fluorochemical containing release materials [28]. The fluorochemical component lowers the surface energy of the release coating, but it also increases the incompatibility between the silicone PSA and the release coating, thereby reducing interdiffusion across the release coating/PSA interface. Alternatively, phenyl groups have been incorporated into the siloxane used in the PSA to provide incompatibility between the silicone PSA and the silicone liner [29]. PSAs often times contain low molecular weight additives such as liquid tackifiers, oils, or surfactants. Depending on the chemical nature of the PSA additives and release coating, these low molecular weight additives may diffuse to the PSA/release coating interface and affect the interfacial adhesion. For example, it has been shown that surfactants used to prepare acrylic emulsions can migrate towards surfaces and interfaces upon aging, thereby changing the adhesion properties of coatings made from the emulsions [30,31].

2.5. Chemical interactions at the PSA/release coating interface

In order to minimize the force necessary to peel a PSA from a release coating, the chemical attractive forces at the PSA/release coating interface must be minimized. The attractive dispersion type forces will always be present; however, other attractive interactions such as polar, acid-base, or hydrogen bonding interactions can be minimized through proper design of the release material and selection of the particular PSA/release material pair. Most polymeric materials used for release coatings are multicomponent or multisegment, with one segment (typically alkyl, fluoroalkyl, or silicone) having low polarity and low surface energy. The low surface energy components accumulate at the coating surface to provide the low adhesion feature. Typically, the other components present in the release material, which have higher surface energy and may have significant polar or acid-base character, are buried underneath the coating surface. These components are often needed to enhance the mechanical strength of the coatings, to ensure anchorage of the coating to the backing, to provide a chemical linking of the release moiety to the polymer backbone, to provide an additional feature such as printability, or to provide reactive sites in the case of materials to be cured on web. In order to achieve a stable release force between the PSA and the release coating, a stable interfacial structure is required so that the higher energy polar segments in the release coating and PSA are kept separated from each other. However, upon contact between the PSA and release coating, restructuring can occur within the PSA and release material near the PSA/release material interface, provided that there is sufficient segmental mobility and that there are specific favorable chemical interactions between the chemical groups in the PSA and the release material to drive the restructuring. Many studies have demonstrated that polymer surfaces can restructure upon contact with another medium [32–38]. In the case of a PSA/release coating interface, such interfacial restructuring can result in a marked increase in the release force with increasing aging time or temperature [19,20,39].

2.6. Weak boundary layers

Another factor that can contribute to the low release force provided by a release material is the presence of a mechanically weak boundary layer at the surface of the release coating [40,41]. Upon peeling the PSA from the release coating, the locus of failure is within this mechanically weak layer, resulting in transfer of material to the adhesive and a subsequent loss in adhesion of the PSA. Although the use of a weak boundary layer may not be the preferred method of achieving low adhesion for PSA release coatings, it can be useful if the amount of transfer is consistent and kept to a minimum [42]. However, in many cases the unintentional or uncontrolled transfer of a weak boundary layer to a PSA results

242

D.J. Kinning and H.M. Schneider

2.7. *Rheological contributions*

Assuming a PSA/release system in which no weak boundary layer exists, prediction of release force and peel character are difficult even if one has knowledge of the chemistry and contact area, the surface energies of both the release and PSA surface, and the interfacial energy of the system. In addition to the rheology of the PSA, the rheology of the release system can play an important role. To illustrate this point, comparison can be drawn between a silicone surface and a well-crystallized alkyl side chain polymer (or self-assembled monolayer), in which only methyl groups are presented at the surface. While the surface energies of these systems are identical at room temperature, and both are non-interacting with the PSA, release from the silicone layer is likely to be smoother and easier than that from the side chain polymer at most peel rates [17,18]. The operative difference between the two release systems considered is flexibility. Alkyl side chain polymers depend on side chain crystallinity to remain non-interacting with the adhesives. PDMS, on the other hand, is a very flexible molecule with a very low T_g , still fluid though viscous at very high molecular weights. It is the flexibility of the crosslinked PDMS network that makes it a superior release system [17,18]. Work with fluorinated materials also dramatically underscores the importance of rheology or flexibility to release. Many comparisons have been made between PDMS and fluorinated release surfaces that show that even though the fluorinated surfaces present lower surface energies, their release is tighter and more likely to be raspy. In comparing PDMS and Teflon, the rougher texture of the Teflon surface is assumed to contribute to the higher release force; however, the dominant contributor is speculated to be the difference in system rheology and interfacial slippage [43,40].

Visual observations by Newby and colleagues [17,18] and others show that the peel front of transparent commercial tapes being removed from PDMS, hydrocarbon and fluorocarbon monolayers is dramatically different. While surface free energies and the spreading coefficient described previously [7], would predict that the release force should be lowest for the fluorinated system, PDMS gives the easiest release. Observational experiments include those in which fluorescent molecules were placed at the adhesive release interface, or within the bulk of the adhesive. During peel from fluorinated layers, particles at the interface did not move appreciably as the peel front approached, but those in the bulk showed large displacements. This indicates friction at the interface and shear dissipation within the bulk, both of which result in high release forces. In contrast, the same PSA on PDMS showed equivalently large displacements of particles ahead of the crack tip, whether at the interface or in the bulk. This implies that interfacial slippage can occur which minimizes shear dissipation within the system. The observations show that on the more flexible PDMS layer, slip is allowed, preventing profound fingering of the PSA and high shear deformation in the region above the crack tip.

The dependence of release force on the flexibility of the release layers is noted in systems other than silicones. Recent work in olefin release shows that release is a strong function of the density or crystallinity of the layer [44]. At a density above 0.9 g/cm³, release for an acrylate PSA is greater than 270 g/cm. However, when the density of PE is dropped to 0.865 g/cm³, the release force of the same adhesive construction drops to 35 g/cm. An investigation of interfacial friction and slip in these systems has not yet been reported, but again the manipulation of release rheology greatly impacts the measured peel force.

3. Release material chemistries

3.1. *Silicone networks*

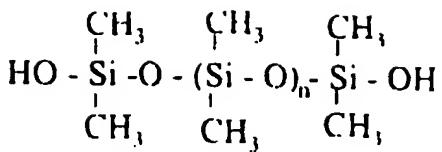
The goal of silicone release liner chemistry is to provide a silicone (polydimethylsiloxane, PDMS) system which can be delivered to a substrate to form a complete thin film, anchored to the backing, and cured such that the PSA can be removed with minimal contamination. Further required is that the release chemistry be tailor able to provide a predictable level of release force for a given adhesive chemistry, with stable release forces over a range of storage time and temperature conditions. From these basic release needs, four major classes of silicone chemistries have evolved, each offering a unique balance of economic and performance advantages. Economic considerations include cure time and energy input, substrate compatibility, processing equipment, raw material costs, environmental concerns, etc. Technological advancements center on tailoring release, release stability, contamination, processing advancements and added functionality.

The oldest of the silicone liner cure chemistries, initially produced in 1955, is the condensation cure system. This system continues to be used and developed, although for environmental reasons is losing favor [23,45,46]. In its most basic form, the release chemistry includes a silanol functional high molecular weight silicone base polymer, a hydride functional crosslinker and a condensation catalyst (i.e. dibutyl tin dilaurate). Additional components can include fast cure additives, bath life extenders, and anchorage additives. The primary components and reaction schemes are shown in Fig. 2. Condensation cure encompasses two basic reactions. The most dominant reaction is that between the silanol and the silyl hydride, forming the siloxane bond and liberating hydrogen. Secondly, silanol ends can react to form the siloxane bond, with water being liberated.

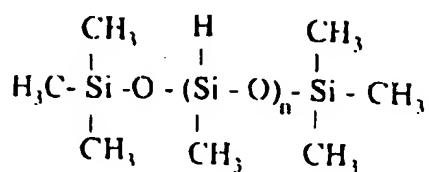
Although waterborne systems were developed in the 1960s, the form of this chemistry that dominates the industry utilizes end-functional, high molecular weight base polymers dissolved in organic solvents. Work on solventless condensation systems continues, but has not yet become commonplace [45,47].

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D.J. Kinning and H.M. Schneider



Base Polymer – n > 500



Crosslinker: n = 10-50

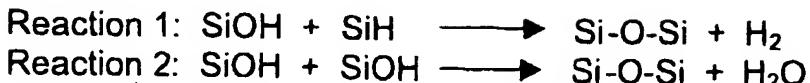


Fig. 2. Primary components and reaction schemes.

cessing, thermal cure during solvent drying, good anchorage to substrate and slippery feel. The major drawbacks are handling of solvent and the pronounced post cure phenomenon, wherein the release chemistry continues to react for hours to days after becoming ‘smear free’. (Post cure and vitrification will be more fully discussed in the section on epoxy silicones.) Cure chemistries developed more recently, discussed in the following paragraphs, eliminate the need for solvent, and increase the cure speed.

Hydrosilation silicones or ‘addition cure’ systems utilize a hydride functional crosslinker with a vinyl functional base polymer and a noble metal catalyst. While the cure can be initiated with UV [48,49], thermal cure versions dominate the commercial market [23,50]. In thermal cure systems, inhibitors are necessary for processing and anchorage additives are common.

Addition cure silicones can be delivered from solvent, waterborne emulsions, or 100% solids systems. The solvent free versions employ base polymers of intermediate molecular weight to achieve processable viscosity. These base polymers can have reactive moieties in terminal and/or pendant positions. These lower molecular weight, more functional systems result in a tighter crosslink network which feels ‘rubbery’ to the hand. Low amounts of high molecular weight additives are included in some formulations to provide a more slippery feel [51,52].

Advantages of the hydrosilation system (Fig. 3) include the elimination of solvent, improved cure speed, and potential for UV or thermal cure. Drawbacks to the system include more expensive multiroll coating methods, potential poisoning of the Pt catalyst (with Sn, S, Cr, amines, etc.), poor anchorage to some films, and a need to carefully balance the hydride to vinyl ratio employed for cure to avoid detrimental interactions with acid containing adhesives [23,53].

Epoxy cured silicones were developed to be photo initiated rather than thermally cured [54]. The chain length of these materials ranges to 200 monomer repeat units, but the majority component of most formulations is significantly shorter. The structure of a typical base polymer is shown in Fig. 4. The chain can be terminal and/or pendant functional, with degree and type of epoxy function-

Release coatings for pressure sensitive adhesives

545

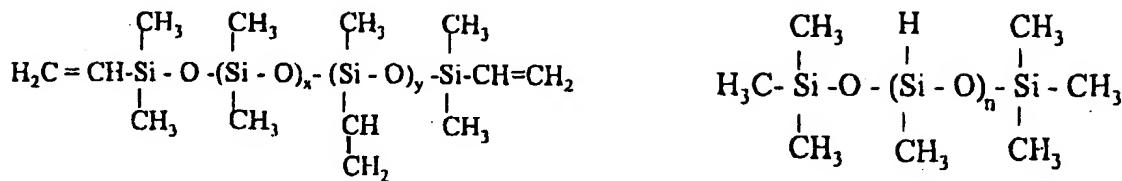
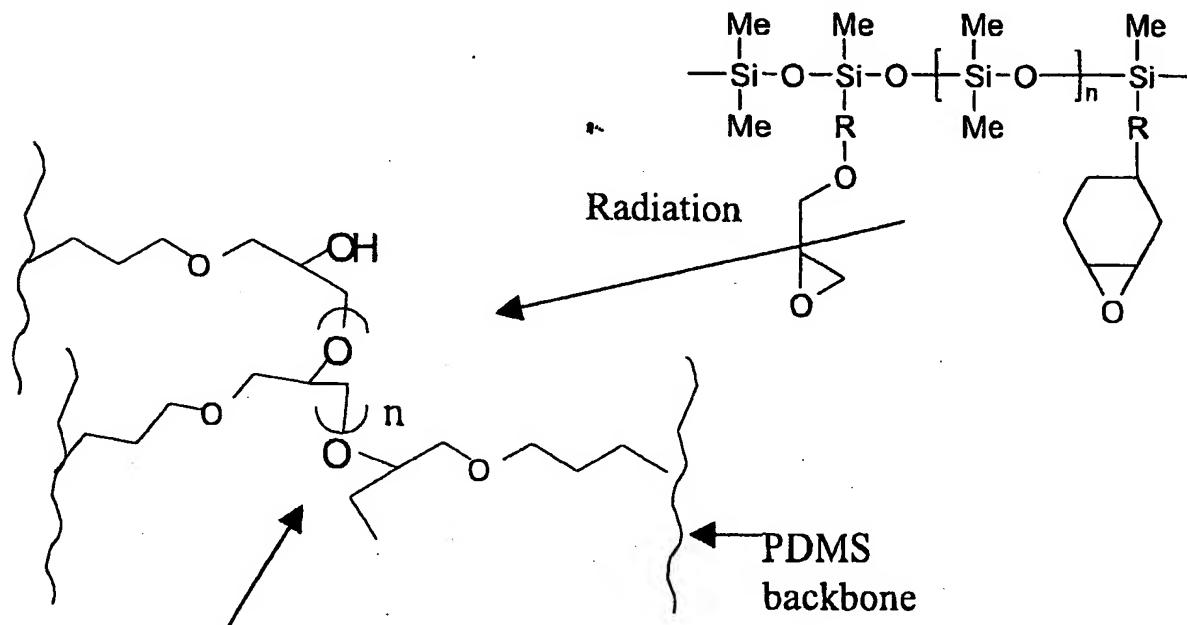
Base polymer: $x + y = 50-400$ Crosslinker: $n = 10-50$ 

Fig. 3. Hydrosilation system.

ality varying by vendor source [54–56]. The release formulations contain one or more types of base polymer, a cationic photoinitiator and a ‘reactive diluent’ chain transfer agent. The formulations while deliverable from solvent or aqueous emulsion [57], are typically coated at 100% solids, eliminating the need for solvent drying. UV irradiation is thus the only energetic cost requirement and the photoinitiator absorbs and reacts during this exposure. The photolysis of the catalyst (several are available [56,58–61]) results in the formation of a sulfur or iodine centered radical, which abstracts a hydrogen to become a strong acid. The cure results from homopolymerization of the epoxy system initiated by protonation of the oxirane ring.

As the system continues to crosslink, ‘vitrification’ occurs which can result



Non-PDMS portion of
crosslinked network

Fig. 4. Epoxy cured silicones.

716

D.J. Kinning and H.M. Schneider

in an extended post-cure similar to that described in the condensation system [23,56]. At this point, the system is sufficiently gelled to drastically constrain mobility. Polymer diffusion to active radical sites is suppressed, leaving unreacted functional groups to interact with subsequent acid containing adhesive coatings. In epoxy systems, alcohols are added as chain transfer agents. Reaction of an alcohol with the oxirane ring converts the immobile oxonium ion to a mobile proton, initiating a new polymer chain. External heat can also aid in driving the reaction to completion. By the proper utilization of chain transfer agent and optional heating, the post cure phenomenon can be minimized in this system.

Epoxy silicones also differentiate themselves from the previous two classes discussed in that variations of the base polymer structure (% PDMS vs. % epoxy) can yield a broad range of release values. Highly functional base polymers exhibit tighter release, more robust anchorage to substrates, and lower Si transfer levels [62,63]. Base polymers that contain more PDMS, and are preferably only terminal functional, are added at low levels to give premium release and smooth peel [56,64,65]. These additives can increase cure times and silicone transfer. Very tight release is possible by blending epoxy silicones with epoxy terminated organic monomers or polymers [66,67].

Advantages of the epoxy systems are the absence of solvent, UV initiated cure that does not require inerting, a wide range of release levels possible and excellent anchorage to film. Disadvantages include cure inhibition on basic substrates and the need to carefully balance formulation cure speed and completeness with release properties.

Silicone acrylate technology, while known since the 1970s [68], has been applied to release coatings more recently [69]. Both homopolymerization of multifunctional silicone acrylates and copolymerization with organic acrylates is practiced [22,70]. Examples of blended systems will be deferred to the next section, understanding that an increase in the non-silicone component acts to increase the release level, analogous to the epoxy system described above.

Silicone acrylates (Fig. 5) are again lower molecular weight base polymers that contain multiple functional groups. As in epoxy systems, the ratio of PDMS to functional material governs properties of release, anchorage, transfer, cure speed, etc. Radiation induced radical cure can be initiated with either exposure of photo initiators and sensitizers to UV light [22,46,71] or by electron beam irradiation of the sample.

Advantages are similar to the epoxy system, in that these can be solventless and do not require thermal energy. Disadvantages unique to this system, however, include the need to inert the cure chamber to avoid air-inhibition of cure as well as some release instability with acrylate adhesives [72].

Silicone release coatings are the workhorses of the easy release industry because the very nature of the molecule fulfills most requirements for low adhesion. When well cured, silicone networks are fairly inert and present a very low sur-

Release coatings for pressure sensitive adhesives

547

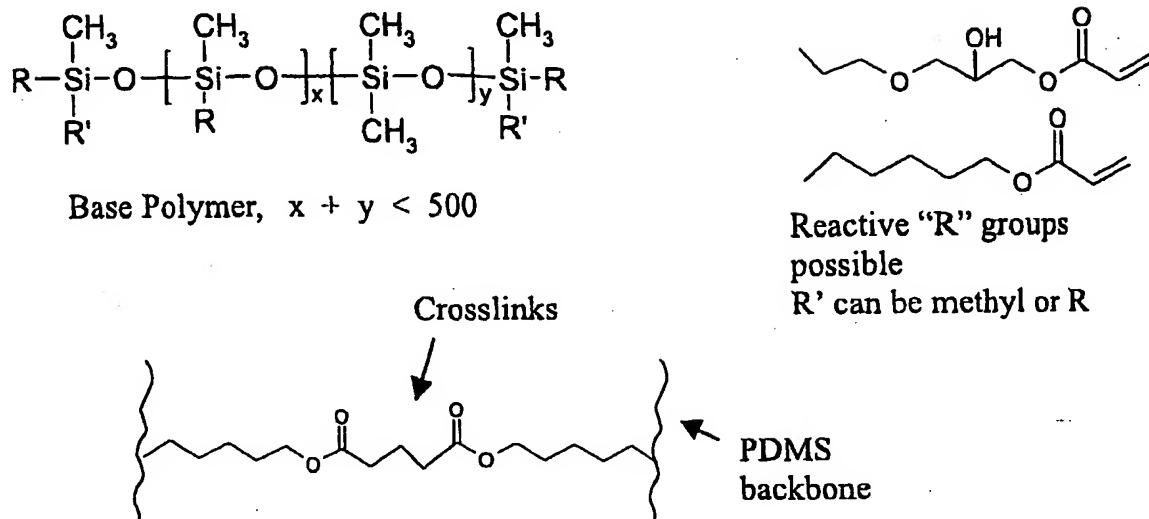


Fig. 5. Silicone acrylates.

face energy. The PDMS backbone presents no opportunity for specific chemical bonding or even acid-base or hydrogen bonding interactions. In condensation and addition cure systems, only unreacted crosslink sites have the potential for chemical interaction, though this can be avoided through appropriate formulation and processing. In epoxy and acrylate systems, the organic segments can act to intentionally increase release, but for low release formulations, this reactive functionality is minimized. The silicone polymer is also fairly immiscible with most organic polymers useful for PSAs. The lack of miscibility prevents extensive interdiffusion and entanglement, again providing easy release. It must be cautioned that if the PSA is applied to the release coating from solution or as a monomer, miscibility improves and some interdiffusion is possible. This phenomenon is also dependent on the crosslink density of the silicone network, with high molecular weight, low crosslink density systems being the easiest to penetrate [21,23]. Additionally, some more loosely crosslinked systems tend to show some rate dependence of release force, with higher separation speeds leading to tighter peel. One hypothesis is that the looser the crosslink network, the more extensible the release system, leading to higher dissipation of energy and therefore higher release forces [23].

When initial PSA/release interactions are minimized in the well cured networks of addition or condensation cured silicones, interfacial restructuring is not a significant problem because the entire network is basically silicone. Under cured systems or high levels of residual hydride functionality can provide specific chemical interactions with acid containing adhesives, leading to acrylic lock-up. However, assuming that the silicone network is properly cured, aging on these surfaces is fairly stable. Epoxy silicones and silicone acrylates are subject to some restructuring, with the non-silicone parts of the molecule mixing favorably with some PSAs. Acrylic PSAs, especially those containing acid, have some potentially

favorable interactions with epoxy or acrylate containing silicones. Increase in release force with aging is thus possible.

A word should be said about the 'weak boundary layer' effect and silicone release [40,41]. Studies have shown that having loose silicone oil that can transfer to the PSA will lower release, however subsequent adhesion will likely suffer as well. In most commercial instances using silicone liners, a weak boundary layer is not intentionally employed. Additionally, many 'low transfer' silicone liners are commercially available which provide premium release and show low to no PDMS transfer to PSAs, indicating that PDMS transfer is not a necessary condition for easy release.

With proper processing and curing conditions, silicones are fairly easy to coat and provide smooth uniform surfaces. Molecularly, silicones are very flexible, providing low friction and the interfacial slippage discussed previously. It is by this molecular flexibility that silicones distinguish themselves, allowing easier release than their similarly low energy, non-interacting organic release counterparts. The flexibility of silicones is curtailed by the addition of organic molecules or silicate resins to provide release tailoring.

Modifying the rheology of silicones is the dominant method of tailoring the release force of silicone liners, again supporting the importance of the rheology of the release system. Controlled release additives are very high T_g methyl-treated silicate resins, also called MQ resins (Fig. 6). Their molecular weight is usually a few thousand, and the resin may be partially functional (OH, vinyl, etc.). In most cases, the resins are dissolved for ease of blending with the silicone formulation before coating. At low concentrations of MQ solution in the formulation, little effect is seen; however, release forces usually increase sharply with MQ level above about 30 wt%. The MQ resins act on the release layer in several ways. To some degree, interactions with the adhesive can be affected, but the effect on the surface energy is not large. Studies have shown that the MQ resin can reduce the segmental mobility of the PDMS chain [73], but that overall effect

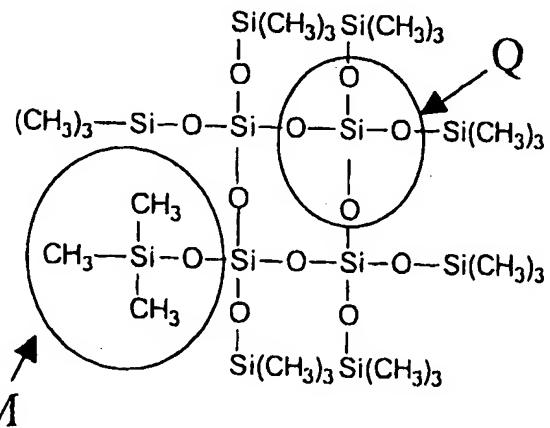


Fig. 6. MQ resin.

should be similar to increasing the crosslink density of the cured network, which is minor. Adding MQ to the silicone network greatly increases the T_g of the release system, which has been shown to correlate with tighter peel and more raspy peel at given peel rates. Studies have shown that both the storage and loss modulus increase, with the greater effect in loss modulus [74]. In addition to the bulk rheological effect, MQ inclusion affects the release surface dynamics as well. The most compelling explanation offered so far again ties back to interfacial mobility and slip. Measurements of slippage for silicone networks containing various amounts of controlled release additive show that adding MQ resin can reduce or even eliminate slip. Interfacial shear measurements also increase markedly with incorporation of MQ resin [75]. Again the argument is that the reduction in flexibility of the silicone network results in increased friction, and a rigid surface which sustains higher stress levels.

3.2. Fluoropolymers

Fluoropolymers are theoretically interesting release systems since very low surface energies can be obtained. Release layers of Teflon®, fluorinated waxes, self assembled monolayers and high molecular weight curable polymers have been evaluated and find very limited success as release for PSAs [18,76]. Fluoropolymers, as mentioned previously, provide low surface energy coatings, but may not be flexible molecules. The lack of flexibility leads to raspy, tighter peel when compared to silicone coatings [17,18]. Fluoropolymer coatings are very expensive, and are therefore usually coated quite thin. These systems tend to be very application dependent, used in markets like healthcare and electronics which can support custom tailoring of adhesive and release formulations.

Several systems comprised of curable perfluoropolyethers [42,77] have been reported. An example of a perfluoropolyether molecule is shown in Fig. 7, with the level of ether linkage, type of curable functional group and overall molecular weight being variable. The curing of the functional groups proceeds as is typical for those chemistries; for example the acrylate functional fluorinated polyether can be cured by UV irradiation as is discussed in the section on silicones. To some extent, the degree of cure completeness is manipulated to control the release level, and an example of using a weak boundary to achieve low release was given previously [42].

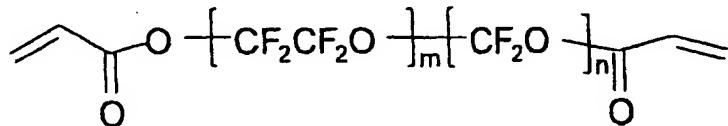


Fig. 7. A perfluoropolyether molecule.

3.3. Fluorosilicones

Fluorosilicones consist of PDMS backbones with some degree of fluoro-aliphatic side chains. The fluorinated group can be trifluoropropyl, nonafluorohexylmethyl, or fluorinated ether side group [78,28,79]. These polymers differ not only in substituent group, but also in the amount of fluoro-substitution relative to PDMS, the overall molecular weight and crosslink density, and the amount of branching. In most commercially available cases, these polymers are addition cure systems and the reactions are those discussed previously for silicone networks.

The mechanisms employed for release in silicones are similar for fluorosilicones. A well crosslinked network provides a very low surface energy and few opportunities for direct chemical interaction between it and the PSA. Fluorosilicones are generally employed with silicone PSAs, in which case the fluorinated side groups act to help make the release polymer immiscible with the PSA. The amount of fluoro-substitution and the length of the fluorinated side group also impact the physical interdiffusion of the release and PSA molecules. To a point, increasing the amount of fluoro-substitution lowers mixing of the molecules and leads to lower peel forces. Restructuring of these networks is possible with time and temperature in the presence of the PSA, and aging can be difficult [80,81].

3.4. Alkyl side chain polymers

Polymers containing long alkyl side chains, typically between 16 and 22 carbon atoms in length, have been used extensively as low adhesion backsizes for PSA tape products for many years. The general structure of such polymers is shown schematically in Fig. 8. The alkyl side chains are attached through a bridging group, R_1 , to the polymer backbone, and the backbone may contain comonomers, R_2 .

In 1950, Dahlquist et al. [82] reported the use of polyvinyl *N*-alkyl carbamates as PSA release materials. Since then, many other types of alkyl side chain polymers have been patented for use as release coatings, including copolymers based on higher alkyl acrylates or methacrylates [83–86], polyvinyl esters of higher aliphatic fatty acids [87], higher alkyl vinyl esters or ethers and a maleic

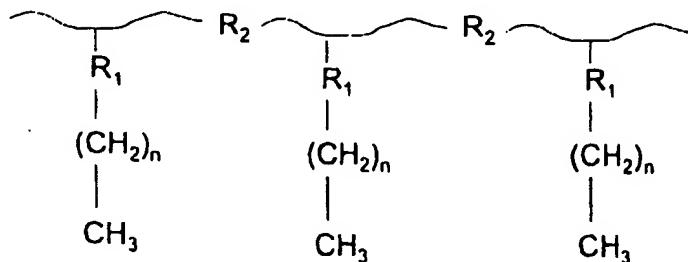
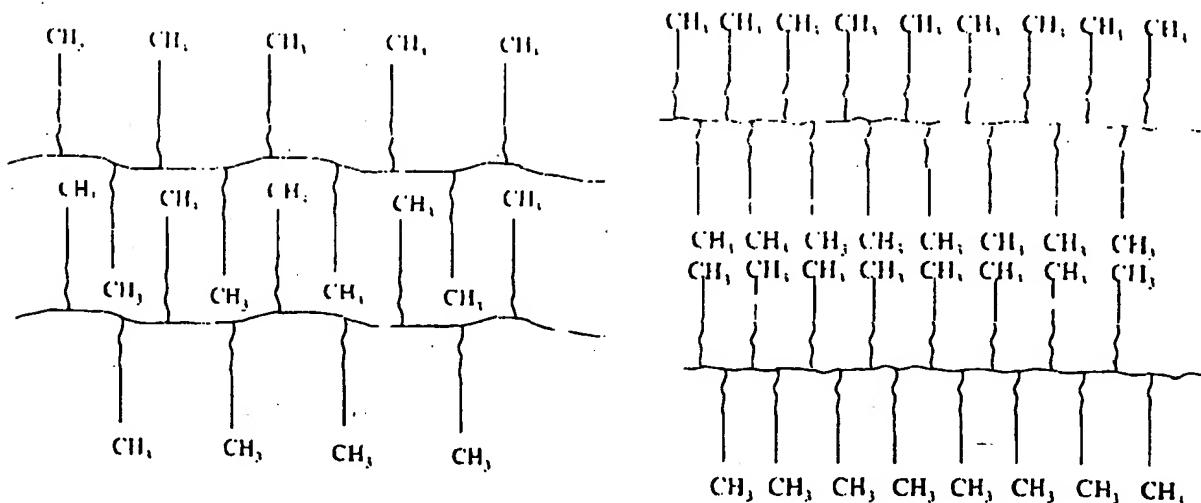


Fig. 8. Alkyl side chain polymers.

acid [88], *N*-alkyl polyacrylamides [89], the reaction product of ethylene-maleic anhydride and higher alkyl amines [90], octadecyl maleamic acid [91], fatty acid itaconates [92], poly-*N*-acyl-imines [93], and polyethylene imines acylated with higher fatty acids [94]. These types of release materials are typically coated from dilute solutions in organic solvents, although those containing acid groups can be dispersed in water by treating with a base, such as morpholine, followed by stripping of the solvents [83,85,88]. Alternatively, certain versions can be made directly in water via an emulsion polymerization process [86]. The alkyl side chain polymers generally provide release forces between about 50 and 500 g/cm, depending on the particular release material chemistry, PSA composition, tape backing, aging condition, etc. Therefore, they are most often used as LABs for PSA tape rolls, rather than for liners. The nonpolar alkyl side chains are attached to the polymer backbone through a bridging group, which is typically a polar group. In addition, the polymer backbone may contain polar segments or comonomers. The nonpolar alkyl groups, in particular the methyl groups on the ends of the alkyl side chains, provide a low energy surface in order to reduce the adhesion, while the polar groups provide mechanical strength and anchorage to backings. In order for such materials to be useful as release coatings, they need to provide stable unwind forces under whatever temperature and humidity conditions the PSA product will experience. In addition, they should ideally provide stable release forces for a variety of different PSA chemistries. While most, if not all, of the previously mentioned patented release materials can provide stable release under room temperature aging conditions, many of these release materials exhibit a significant increase in release force when aged at higher temperatures. For example, Williams et al. [87] reported that the low adhesion properties of polyvinyl stearate based copolymers were lost when aged against rubber-resin PSAs at temperatures above their melting points (35–43°C). Smith [92] reported that the release force of a rubber-resin based PSA tape, peeled from a poly stearyl itaconate release coating, increased from 60 g/cm when aged at room temperature to over 530 g/cm when aged at 65°C. In order to overcome this type of aging instability, Grossman et al. [91] developed release materials having melting points much higher than any aging temperature the tape might experience. For example, a copolymer of octadecyl maleamic acid with methyl acrylate, which had a melting point of 105–110°C, gave an initial release force of 75 g/cm and a 1 week 65°C aged release force of only 100 g/cm for a rubber-resin type PSA. In addition, Dahlquist et al. [82] mention that polyvinyl carbamates containing residual hydroxyl groups can be chemically crosslinked with a small proportion of a diisocyanate, thereby increasing their heat resistance (softening points).

X-ray scattering studies have shown that polymers containing long alkyl side chains typically form alternating layered structures in the bulk, with the polymer backbone forming one layer and the alkyl side chains forming the other layer —————— in Fig. 9. Generally, for side chain lengths



Single Layer Packing

Double Layer Packing

Fig. 9. Polymers containing long alkyl side chains typically form alternating layered structures.

greater than about 10–12 carbon atoms, the side chains will crystallize with hexagonal packing and be oriented, more or less, perpendicular to the backbone layer [95–97]. As would be expected, increasing the length of the alkyl side chain results in an increase in the layer spacing. Thermal studies have shown that only the portion of the side chain beyond the first 10–12 carbon atoms is involved in the hexagonal packing [98]. Typically, alkyl side chain polymers used for release coatings contain side chains of about 18 carbon atoms in length, in order to have sufficiently high melting points. As shown schematically in Fig. 9, both one-layer and two-layer packing have been observed depending on the specific chemical structure and the thermal history of the material [97], with the two-layer packing exhibiting slightly higher melting temperatures. Generally, decreasing the distance between the side chains along the backbone or increasing the flexibility of the polymer backbone favor two-layer packing. The melting point of these side chain polymers usually increases with increasing side chain length [95,96]. For example, the melting points of poly (*n*-alkyl acrylates) are about 32°C, 43°C, and 56°C for alkyl side chains having 14, 16, and 18 carbon atoms, respectively [96]. The melting point also tends to increase with increasing side chain content [97,99,100], increasing flexibility of the backbone [99,101,102], or annealing [96].

Polymers with long (e.g., 18 carbons) alkyl side chains have often been shown to possess surface energies that are similar to that of a monolayer of methyl groups (23 mJ/m²), indicating that the methyl groups on the ends of the side chains can pack effectively at the polymer surface [19,103,104]. The surface energy has been found to decrease steadily as the length of the side chain is increased, at least up to a side chain length of 10–12 carbons [103,104] where the side chains start

to crystallize. At the higher side chain lengths, lower surface energies have been reported in the cases of higher side chain content and higher backbone flexibility [103]. Note that these are the same factors that promote higher melting points in the bulk, indicating a correlation between the surface and bulk packing of the side chains. It is evident that the layered structure present in the bulk can persist at the polymer surface, with the alkyl side chains oriented nearly perpendicular to the surface.

In order for release materials to provide stable release forces for pressure sensitive adhesives, a stable interfacial structure is required so that the higher energy or polar segments in the release coating and PSA are separated from each other. However, upon contact between the PSA and the release coating, restructuring can occur within the PSA and release material near the PSA/release material interface, provided that there is sufficient segmental mobility and that there are specific favorable chemical interactions between the chemical groups in the PSA and the release material to drive the restructuring. The crystallization of the alkyl side chains provides a means by which the segmental mobility of the side chain release polymer can be greatly reduced [19,105]. The initial low surface energy structure of the release coating can then be preserved upon contact with the PSA, leading to stable release forces. Therefore, the melting point of the alkyl side chain polymer can play an important role in determining the release performance as a function of aging temperature.

Kasemura et al. [106] studied the surface dynamics, at room temperature, of the alkyl side chains in poly(vinyl alkylate)s using dynamic contact angle methods. In the case of alkyl side chains having 6 to 12 carbon atoms, the surface mobility is quite high and a large hysteresis between the advancing and receding water contact angle is seen. However, for higher side chain lengths, between 14 and 18 carbons in length, where the side chains crystallize, the hysteresis was greatly reduced due to a lower segmental mobility.

Kinning [19] studied the bulk, surface and interfacial structure of copolymers of polyvinyl *N*-alkyl carbamates and vinyl acetate (1 : 1 molar ratio), having either 10 or 18 carbons in the alkyl side chains, using thermal analysis, X-ray scattering, contact angle analysis, X-ray photoelectron spectroscopy (XPS), and static secondary ion mass spectrometry (SSIMS). While both polymers exhibited an overlayer of the alkyl side chains at the polymer surface and a surface energy typical of a monolayer of methyl groups, the release force profiles for the two polymers were quite different. The decyl version was unable to maintain a stable release force against an acidic acrylate PSA at any aging temperature, while the octadecyl version was able to provide stable release at aging temperatures less than about 50°C. The increase in release force was shown to be a result of interfacial restructuring, whereby the concentration of basic urethane and vinyl acetate groups in the release coating increased at the interface with the acidic PSA, leading to increased acid-base interactions and higher adhesion. In the case of

octadecyl side chains, side chain crystallization was apparent with a melting range of about 45–65°C, resulting in reduced segmental mobility and stable release forces at temperatures at least as high as 50°C. In contrast, the decyl version did not exhibit side chain crystallinity, only a glass transition centered at about 48°C. It is interesting to note that stable aging was not obtained for the decyl version at a temperature nearly 30°C less than the backbone glass transition temperature. Crystallization proved much more effective at locking the original surface structure in place, upon contact with the PSA, than having a high glass transition temperature.

Cai et al. [105] studied the surface and adhesion properties of undecyl oxazoline homopolymers as well as undecyl/phenyl oxazoline copolymers. Such polymers had relatively high melting points of between 135°C and 145°C, due to the fact that the polymer crystallizes into a triclinic unit cell involving both the backbone and side chain segments [107]. Contact angle and XPS analyses indicated that the undecyl side chains were oriented towards the surface, with the methyl endgroups covering the surface. In Cai's study, the peel forces of Scotch™ Brand Magic tape from coatings of the undecyl oxazoline polymers were quite low, increasing from an initial value of about 5 to about 12 g/cm after aging for 2 days at room temperature. The low peel forces could be maintained at aging temperatures approaching the melting point of the undecyl oxazolines. The increase in peel strength at aging temperatures near, or above, the melting point was attributed to the undecyl oxazoline coating dissolving into the PSA, once it melted. Alternatively, the melting of the undecyl oxazoline, and the concomitant increase in segmental mobility, could have resulted in an interfacial restructuring at the PSA interface, leading to attractive acid–base interactions between the basic amide groups in the release coating and the acidic groups in the PSA. Block copolymers of undecyl/phenyl oxazoline exhibited much higher peel forces than the undecyl oxazoline homopolymer. In addition, the peel forces increased significantly with aging time, even at low aging temperatures. The authors attributed this behavior to an incomplete coverage of the block copolymer surface with the undecyl groups.

Cai and Litt [108–110] also studied the surface and adhesion properties of random copolymers made from pentamethyl disiloxanyl decyl oxazoline and undecyl oxazoline. For these copolymers the melting point and crystalline content decreased steadily as the content of pentamethyldisiloxanyl groups increased. The critical surface tensions of the copolymers were measured to be 21 mJ/m² for all the copolymers, indicating that the amide groups in the polymer backbones were buried and the methyl groups covered the surface. The copolymers with less than 50 mol% pentamethyl disiloxanyl decyl oxazoline showed good release properties towards Scotch™ Brand Magic tape at aging temperatures of 50°C or less. However, the peel strengths increased dramatically as the aging temperature approached the melting points of the copolymers. Again, the melting of the release

polymer, and the concomitant increase in segmental mobility, likely resulted in an interfacial restructuring at the PSA interface, leading to attractive acid-base interactions between the basic amide groups in the release coating and the acidic groups in the PSA.

As mentioned previously, alkyl side chain polymers typically do not provide low enough release forces for most liner applications, in spite of having surface energies similar to the siloxane coatings that can provide very low release forces. This difference may be due, in part, to differences in bulk and surface rheology. Because the alkyl side chain polymers usually rely on crystallinity to provide stable release properties, they are typically high modulus materials. In contrast, polydimethylsiloxanes have a much lower modulus and a lower coefficient of friction which have been shown to be important factors in determining release force [17,18]. In general, the type of polymers which provide the easiest release tend to have low modulus.

3.5. Fluoroalkyl side chain polymers

Polymers containing fluoroalkyl type side chains have also been used as release coatings for PSAs, though not as extensively as alkyl side chain polymers. Such polymers can form ordered layered structures in the bulk similar to those seen for alkyl side chain polymers [111]. Volkov et al. [112] studied the structure of perfluoroalkyl side chain polymers having $-C_8F_{17}$ endgroups on the side chains, and found that increasing the main chain flexibility, on going from polyfumurate to polymethacrylate to polyacrylate enhanced the ability to form an ordered structure. The polyfumurate was amorphous, the polymethacrylate showed an ordered layered structure of the backbone without hexagonal packing of the side chains (Smectic A type liquid crystalline structure), and the polyacrylate showed both an ordered layering of the backbone and a hexagonal packing of the side chains (Smectic B type liquid crystalline structure). X-ray scattering studies indicated that a transition from the Smectic B liquid crystalline structure to the isotropic state occurred at a temperature of 77°C.

It has long been known that polymers containing fluorinated side chains can exhibit extremely low surface energies. For example, Bennett and Zisman [113] showed that polymers having $-C_7F_{15}$ and $-C_8F_{17}$ containing side groups had critical surface tensions of 10–11 mJ/m², nearly as low as the critical surface tensions of perfluoroalkanoic acid close packed monolayer [114]. It was proposed, therefore, that the fluorinated side chains were oriented nearly normal to the surface and nearly close packed, with the $-CF_3$ groups covering the surface.

Pittman and Ludwig [115] studied the wetting properties of a series of fluoroalkyl acrylates having $-CH_2(CF_2)_nCF_2H$ side chains, where n was 1, 3, 5, 7, or 9. The acrylates with $n = 7$ and 9 were partially crystalline (attributed to

113°C, as determined by DSC. These polymers exhibited surface tensions of 13 and 15 mJ/m², respectively, similar to that of the corresponding acid monolayer. It was also shown that these polymers exhibited a sudden change in wetting behavior (decrease in hexadecane contact angle) near their melting points, which was attributed to a transition from a surface dominated by -CF₂H groups below the melting point to a surface dominated by -CF₂- groups above the melting point. Pittman et al. [116] later studied the wetting properties of polymers with -CH₂(CF₂)₆CF₃ containing side chains on one or three out of every four carbon atoms along the backbone. Critical surface tensions as low as 7.5 mJ/m² were reported.

Yokota and Hirabayashi [117] studied the structure of fluoroalkyl methacrylate homopolymer having -CH₂CH₂(CF₂)₇CF₃ side chains as well as alternating copolymers with butadiene. Even with a fluoroalkyl side chain on only every sixth carbon atom along the backbone these copolymers had a critical surface tension of 10.6 mJ/m², similar to the earlier results of Bennett and Zisman. Evidently, the fluoroalkyl side groups were able to pack effectively at the surface even though they were fairly widely spaced along the backbone.

In spite of their very low surface energies, fluoroalkyl side chain polymers are not used as extensively as alkyl side chain polymers for PSA release coatings since they often have a tendency to exhibit unstable release forces upon aging. For example, Dixon [118] reported the use of terpolymers of *N*-ethyl perfluorooctyl sulfonamido ethyl methacrylate, acrylic acid, and alkyl acrylates or methacrylates as low adhesion backsize coatings for paper backed (masking) tapes with various types of PSAs. In these terpolymers the fluorochemical monomer provides the low surface energy and release feature, the acrylic acid provides polarity for anchorage to the tape backing, and the alkyl (meth)acrylate provides solubility in organic solvents. It was reported that a high softening point, preferably greater than 100°C, was needed in order to obtain good release performance. In one example (55/40/5 weight ratio of *N*-ethyl perfluorooctyl sulfonamido ethyl methacrylate/acrylic acid/octadecyl acrylate), the release force for a tackified natural rubber type PSA was 180 g/cm initially and built to 445 g/cm after 7 months of natural aging. This same polymer provided a relatively high release force of 290 g/cm for an iso-octyl acrylate/acrylic acid PSA after aging at 50°C for 11 days, the only aging condition tested. In spite of the very low surface energy of coatings made with this terpolymer, the coatings do not provide either low or stable peel forces. It was reported by Ramharack and Nguyen [119] that the homopolymer of *N*-ethyl perfluorooctyl sulfonamido ethyl methacrylate does not exhibit crystallinity, rather a glass transition centered at about 75°C was observed by DSC. Therefore, the terpolymer discussed by Dixon is not expected to exhibit side chain crystallinity either. This lack of side chain crystallinity probably accounts for the lack of release force aging stability, as the original near surface structure of the release coating is not effectively locked in place upon contact with the PSA. Rather, some degree of

interfacial restructuring likely occurs leading to increased chemical interactions at the PSA/release coating interface.

As discussed by Wang et al. [120], fluorinated block and segmented copolymers typically exhibit surface restructuring upon contact with a polar medium, whereby the amorphous fluorinated surface groups move away from the interface and the polar groups move towards the interface. This interfacial restructuring has limited the practical applications of such copolymers; however, recent studies have suggested methods to provide stable interfacial structures. For example, Maekawa et al. [121] reported that stable low energy surface structures could be obtained for perfluoroalkyl alkyl acrylates having high melting points. Such polymers had $-(CF_2)_nCF_3$ endgroups on the side chains with $n \geq 8$, and could maintain a high water receding contact angle. Wang et al. [120] demonstrated that stable low energy surface structures could be obtained for certain poly(styrene-*b*-semifluorinated side chain) block copolymers. By controlling the block copolymer composition and the relative lengths of the fluorocarbon and alkyl units in the side chain, the effect of chemical structure on the surface properties and the influence of liquid crystalline structure of the semifluorinated side chains on the surface behavior were evaluated. In the case of shorter fluorocarbon units in the side chains (i.e., $-(CF_2)_6-$), a Smectic A phase formed with a critical surface tension of 10.8 mJ/m^2 , and the polymer surface could undergo significant restructuring when immersed in water. In contrast, when the side chains contained $-(CF_2)_n-$ units with $n > 8$, a more highly ordered Smectic B phase was formed having lower critical surface tension (8 mJ/m^2) and a much more stable surface structure. Morita et al. [122] studied the surface properties of perfluoroalkylethyl acrylate/*n*-alkyl acrylate copolymers having about 60 wt% perfluoroalkylethyl acrylate. The perfluoroalkylethyl acrylate had a $-(CF_2)_8CF_3$ endgroup and the length of the alkyl group in the *n*-alkyl acrylate was varied from one carbon (methyl acrylate) through 18 carbons (octadecyl acrylate). Copolymers prepared with *n*-alkyl groups containing less than 12 carbon atoms exhibited a large hysteresis in water contact angle; however, in the case of 16 or 18 carbon atoms in the *n*-alkyl group a high receding contact angle could be maintained due to the crystallization of both the perfluoroalkyl and alkyl side chains. XPS on freeze dried surfaces showed that the contact angle hysteresis, in the case of the shorter alkyl acrylates, was due to a reorientation of the fluorocarbon side chains when the surface was exposed to water. The crystallization of the side chains greatly decreased the segmental mobility in the near surface region of the coatings, resulting in a more stable surface structure. For the copolymer based on stearyl acrylate, a sudden decrease in the receding water contact angle was observed to occur as the temperature was raised beyond the copolymer's melting point (48°C), indicating that the surface molecular mobility reflects the bulk molecular mobility.

Dabroski [123] reported the use of waterbased release coatings based on blends of a small amount of a perfluoroalkyl-alkyl acrylate polymer with a film forming

polymer emulsion. For example, a blend of only 0.8% perfluorinated ester polymer (Scotchban™ FC-824) with an acid modified EVA emulsion provided a 10 day room temperature aged unwind of 160 g/cm for a masking tape based on tackified natural rubber PSA. After 10 days aging at 50°C, the unwind only increased to 180 g/cm. The mechanism by which a stable release force was obtained was not discussed.

3.6. Silicone-organic copolymers and networks

As discussed previously, crosslinked silicone networks are widely used as release coatings for liner applications where premium release (1–10 g/cm) is required. Such release coatings typically provide release forces which are too low for tapes in roll form, however. If the unwind forces are too low, telescoping, flagging, or premature unwinding of the tape roll can occur. For many aggressive PSAs, alkyl and fluoroalkyl side chain polymers typically have difficulty providing unwind forces less than about 80 g/cm. In order to bridge the gap between the release forces obtained with pure, or nearly pure, silicone networks and the side chain polymers, various silicone containing copolymers and networks have been developed. By adjusting such parameters as the silicone content, the silicone block or segment length, as well as the chemical composition of the non-silicone components, the release force can be adjusted as desired for a particular PSA or application. In addition, the wide range of compositions and molecular architectures that can be obtained with these silicone containing polymers allows other functionalities such as printability, writeability, and smooth unwind to be attained.

Various patents discuss the use of vinyl-silicone copolymers, and blends thereof, as PSA release coatings [124–127]. For example, Clemens et al. [124] discloses silicone grafted copolymers prepared from polydimethylsiloxane macromonomers (molecular weights between 1000 and 50,000) having vinyl endgroups and various vinyl monomers such as butyl methacrylate and acrylic acid. The polar comonomer provides anchorage to tape backings. A high degree of incorporation of the silicone grafts is needed to ensure a low level of silicone transfer to the PSA and good readhesion. Controlled and predictable release force is achieved through variation of the number and length, e.g., the molecular weight, of the polysiloxane grafts in the copolymer, as well as the composition of the vinyl backbone. Relatively small concentrations of silicone, usually less than 10%, are required to obtain efficient release since the low energy siloxane segments are highly surface active. Both solvent based and water based versions of vinyl-siloxane copolymers have been described. In addition, some of these compositions are reported to be writable [127].

The use of small amounts (0.5–3%) of polyethylene-polydimethylsiloxane or polystyrene-polydimethylsiloxane block copolymers in blends with a host

polymer have also been disclosed as PSA release coatings [128]. These blends can be extruded as a single layer or coextruded with a backing polymer to form, for example, a backing for PSA tapes. Relatively low copolymer molecular weights (e.g., between 2000 and 10,000) are preferred so that the copolymer can diffuse efficiently to the blend surface upon extrusion. A wide range of release forces can be obtained, depending on the amount and composition of the block copolymer. In the case of copolymers containing polyethylene blended into a polyethylene host matrix it is proposed that the polyethylene block in the copolymer can cocrystallize with the polyethylene matrix, thereby locking the copolymer onto the blend surface and decreasing the extent of silicone transfer to the PSA. However, the readhesion values reported are only between 48% and 73% of the control, consistent with a relatively high level of silicone transfer.

Various types of polyurea or polyurea/urethane segmented copolymers containing silicone segments have also been described as PSA release coatings [129–132]. Again, by adjusting the silicone content, silicone block length, and composition of the non-silicone segments the release force can be tailored for a specific PSA. The polar hard segments in these materials provide anchorage to backings, improved mechanical properties of the coatings, and modification of the release force, while the siloxane segments provide the low energy surface needed for release.

Silicone containing copolymeric networks, wherein a mixture of a functional silicone and copolymerizable monomers or oligomers are coated onto a web and cured, have also been used as PSA release coatings. Various chemistries, including polyurethane/urea–silicone networks [133], (meth)acrylate functional silicones coreacted with other vinyl monomers [134–136], and epoxyfunctional silicones coreacted with vinyl, epoxy, or hydroxy functional monomers [66,137, 138] have been disclosed. Again, depending on the silicone content, silicone segment molecular weight, and composition of the non-silicone component, the release force can be tailored for a specific PSA. Usually, only small amounts of silicone are needed in the case of release coatings for tape rolls. A high degree of incorporation of the silicone segments into the network is required for good readhesion.

There have been many studies concerning the surface structure of various silicone containing copolymers and networks, including polydimethylsiloxane–polystyrene diblock and triblock copolymers [139,140], polydimethylsiloxane–polyvinyl alcohol graft copolymers [141], multiblock copolymers of bisphenol A polycarbonate and polydimethylsiloxane [142], diblock copolymers of polydimethylsiloxane and Nylon 6 [143], polydimethylsiloxane–polyamide multiblock copolymers [144], polydimethylsiloxane grafted polyurethanes [145], polydimethylsiloxane grafted acrylate copolymers [146], polydimethylsiloxane–polyethyleneoxide networks [147], and polydimethylsiloxane containing polyurethane, polyurea, or polyisobutylene urea segmented copolymers [70 148–152]. It has been consistently

D.J. Kinning and H.M. Schaefer

found that the surfaces of films prepared from such materials are dominated by the polydimethylsiloxane blocks or segments even at only a few percent siloxane, due to the low surface energy of the siloxane segments. Often times the polydimethylsiloxane segments form a thin overlayer (10–100 Å) on the surface, with the thickness of the overlayer increasing with increasing silicone content and increasing silicone segment molecular weight. Other factors can also play a role in determining the surface silicone concentration or silicone overlayer thickness including the molecular architecture, the degree of incompatibility, and processing conditions (e.g., choice of casting solvents and thermal history). Like other types of copolymers, silicone containing copolymers have also been shown to undergo interfacial restructuring upon contact with a polar medium such as water [20,141,145,148,152], whereby the silicone segments migrate away from the interface and the more polar or hydrophilic segments migrate towards the interface.

Hsu et al. [146] studied the effect of siloxane content (0.1–10 wt%) and siloxane molecular weight (500–25,000) on the surface composition and PSA release characteristics of a series of siloxane grafted butyl methacrylate/acrylic acid copolymers. Surface analysis by XPS showed that the amount of silicone in the near surface region increased with increasing bulk silicone concentration, leading to decreased peel forces for both rubber based and acrylic based PSA tapes. The release force was also found to decrease with increasing siloxane graft molecular weight, especially at graft molecular weights between 500 and 5000. By changing the silicone content and molecular weight, the silicone concentration near the surface could be easily adjusted, leading to tailored release forces for a variety of PSAs.

Kasemura et al. [153] studied blends of siloxane grafted methylmethacrylate/glycidylmethacrylate copolymer additives coreacted with epoxy resin. The relatively low molecular weight copolymer additives contained 15% of a 5000 molecular weight siloxane macromonomer and various glycidylmethacrylate contents. It was expected that the low surface energy siloxane segments would cover the surface of the blend and the glycidyl groups would coreact with the epoxy resin during curing. Only small amounts (about 1%) of the siloxane additive were needed to obtain a highly siliconized surface and low peel forces for a PSA tape. While the surface concentration of silicone was not affected by the glycidyl methacrylate content in the additive, the peel forces increased systematically with increasing glycidyl methacrylate content. Since no readhesion measurements or surface analysis of the PSA and release coatings were made after peeling them apart, it is difficult to determine the exact mechanism for the observed increase in peel force.

Kinning [20] studied the bulk, surface, and interfacial structures of a series of polyureas containing polydimethylsiloxane segments. In this study, the siloxane segment molecular weight (5000) and content (25 wt%) were kept constant, while

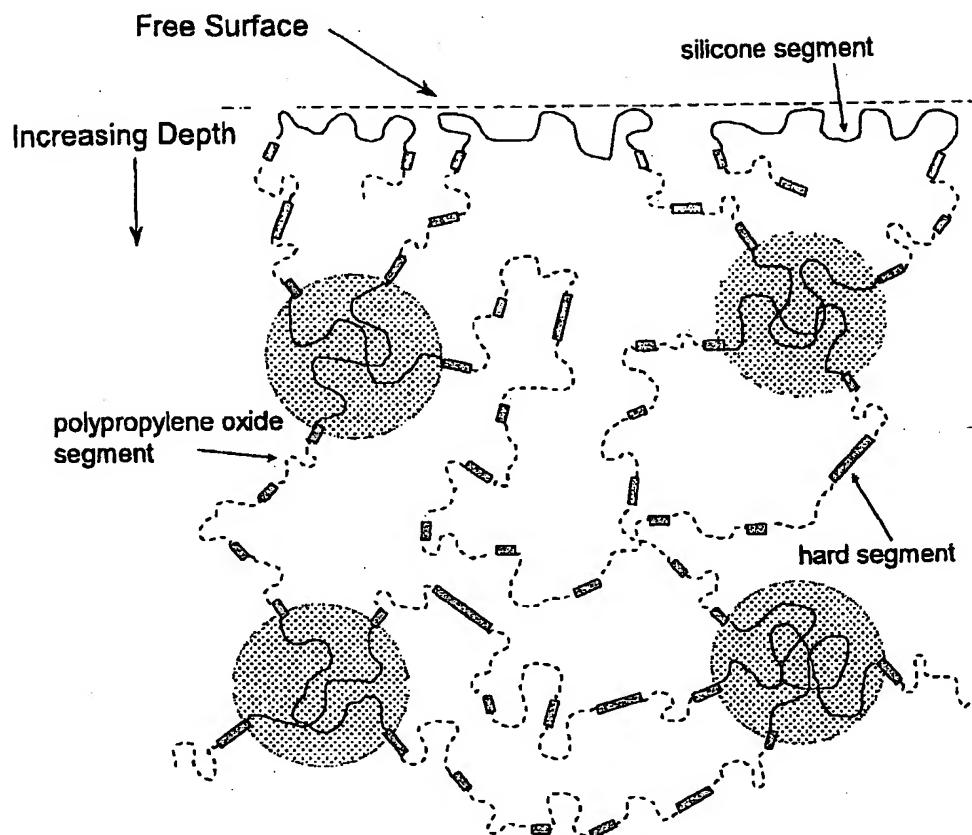


Fig. 10. Silicone polyurea near-surface structure prior to PSA contact. (From Ref. [20], copyright ownership by Overseas Publishers Association, reprinted with permission from Gordon and Breach Publishers.)

the non-silicone segment composition was adjusted in order to obtain a series of materials having a range of glass transition temperatures (between -1 and 170°C) for the non-silicone matrix phase. Surface analysis by XPS, SSIMS, and contact angle analysis showed that all of the silicone polyureas exhibited a thin overlayer, 15–20 Å thick, of the siloxane segments at the coating surfaces, consistent with other studies of siloxane containing copolymers. The release force of a PSA tape containing an alkyl acrylate/acrylic acid copolymer PSA was measured as a function of aging time and temperature. Initially, the release forces provided by the various silicone polyureas were quite low, similar to that provided by silicone based liners. However, the release forces were observed to increase with increasing aging time and/or increasing aging temperature. Silicone polyureas with higher non-silicone matrix phase glass transition temperatures exhibited a slower rate of adhesion build. The build in adhesion was shown to be due to an interfacial restructuring at the PSA/silicone polyurea interface, whereby the non-silicone segments in the silicone polyurea (e.g., the urea groups) migrated towards the interface and the silicone segments migrated away from the interface, as shown schematically in Figs. 10 and 11.

In the case of an acrylate PSA containing an acidic comonomer, there is the

562

D.J. Kinning and H.M. Schneider

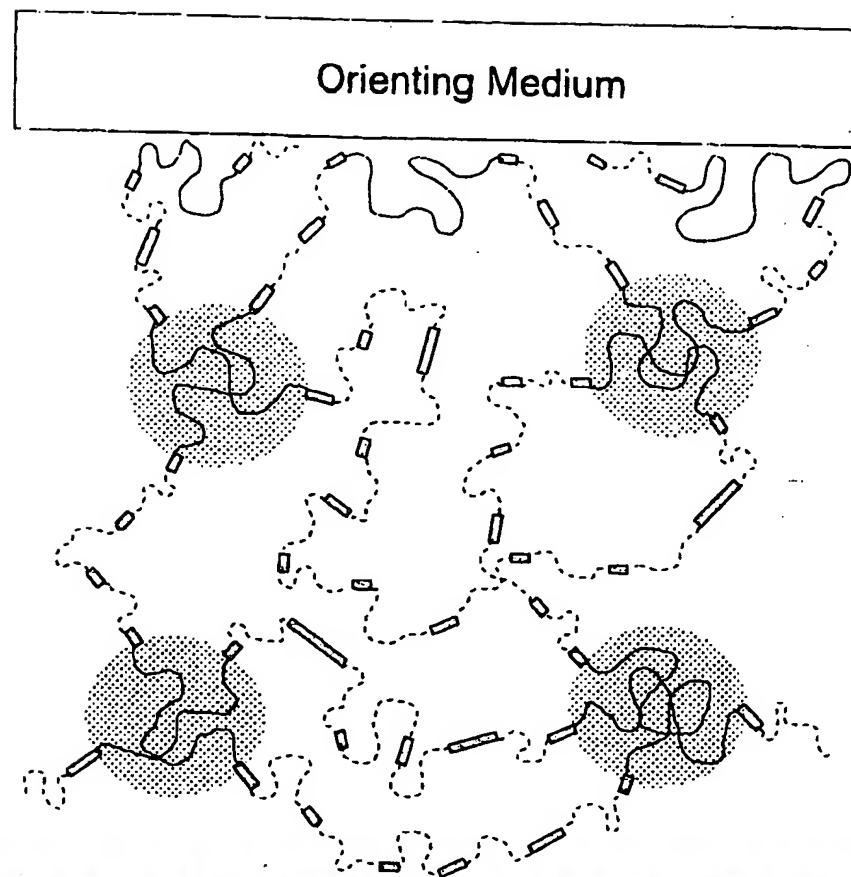
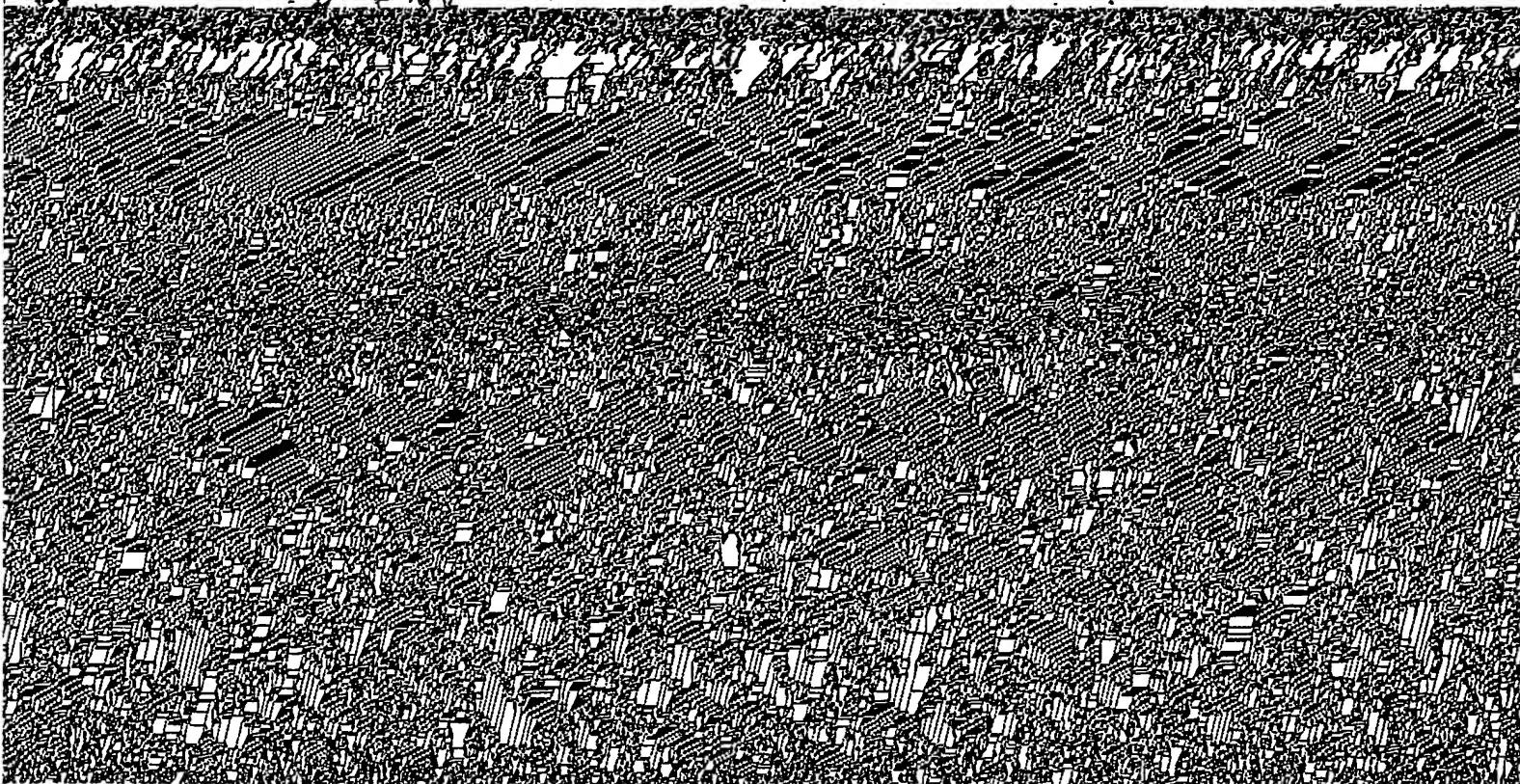


Fig. 5-34



Thanawala and Chaudhury [39] studied polydimethylsiloxane elastomers modified by reacting allyl amide functional perfluorinated ether segments to the siloxane network by a hydrosilation reaction. Only 1–2 wt% of the surface active perfluorinated ether was needed to reduce the surface energy of the elastomer from 22 to 8 mJ/m². However, the addition of the perfluorinated ether to the siloxane network actually resulted in a significant increase in the peel force of an acrylic PSA tape, measured after a short contact time at room temperature. It was also found that the water contact angle hysteresis increased markedly with increasing amount of the perfluorinated ether. These results were attributed to an interfacial reconstruction, whereby the high energy amide functionalities of the perfluorinated ether (originally buried beneath the surface) were attracted to the interface where they could interact with the water or the PSA. The addition of the perfluorinated ether to the siloxane network was therefore proposed as a way of tailoring the PSA release force. No measurements of the effect of aging time or temperature on the release force were reported, however.

3.7. Polyolefins

The use of polyolefins as release materials evolves naturally from the inherent difficulty most PSAs have in adhering to them [154]. Polyethylene (PE) and polypropylene (PP) substrates, when not surface treated (i.e. by corona or flame, etc.) present low energy surfaces, that for some PSAs result in low enough adhesion values to become their means of delivery. Olefin release materials also present fairly non-interacting surfaces. Again, release is only stable where interdiffusion with the PSA is avoided, making olefin release materials inappropriate for most olefin PSAs. Polyethylene used as release materials can be of the high, medium, low or ultra low-density variety. Most current commercial uses of olefins as release components target higher release levels. However, as mentioned previously, manipulation of resin density can lower the release of some PSAs by an order of magnitude. In general, branching of the polyethylene molecule can be used to control the crystalline content or density of the PE film. Additionally, copolymerization with an α -olefin like propylene, butene, pentene, hexene, methyl-pentene or octene via metallocene or traditional catalysis is possible [44,155–157]. In some more recent developments, acrylates copolymerized in the system act to lower the density and also provide reasonable release [158].

Olefins when used as release materials are commonly extruded either as the complete release film or as a skin layer on a multi-layer system. Processing effects can impact the release force in as much as temperatures and orientation can effect crystallinity and density. The polymers are of high enough molecular weight to be sufficiently entangled, and curing is not required. In multi layer systems it is often important that there be tie layers or some priming technique involved to ensure adequate anchorage between the releasing system and the bulk of the substrate.

4. Additional functionalities

As mentioned in the introduction, release coatings are often required to perform other functions besides providing an appropriate release level for the PSA. For example, a tape user may want to write on the release coated tape backing with a pencil or pen. It may also be desirable to be able to print a logo or message directly onto the release coated backing of a tape or a label. In the case of a masking tape used to paint an automobile, the paint needs to adhere to the tape backing when the tape is removed so that the paint does not flake off onto the freshly painted surface. In some cases, for example a tape used to attach a baby's diaper, quiet or smooth release is a desirable feature. In other cases, such as a liner for a transfer PSA, a low coefficient of friction of the release coating can make the PSA application easier.

Typically, writeability, printability, or paintability can be obtained by blending or coreacting a release component with an ink or paint receptive component that can be swollen by, or be dissolved into, the carrier for the ink or paint. Such coatings should not exhibit any dewetting of the ink or paint, and the ink or paint should adhere well enough to the release coating such that it cannot be smeared, rubbed, or flaked off. Mertens et al. [127] disclose the use of siloxane grafted release materials comprising free radically polymerizable vinyl monomers, hydrophilic comonomers, and a siloxane macromonomer for PSA release coatings that can be written on with pens containing either solvent or water based inks. Mertens et al. teach that the incorporation of a hydrophilic comonomer, such as acrylic acid, methacrylic acid, hydroxyethylacrylate, or *N*-vinyl pyrrolidone, results in coatings that can be written on with pens using water based inks due to the water being absorbed into the coating, which facilitates a rapid restructuring of the release coating surface. Initially, the surface is covered with the siloxane segments, but after contact with the water based ink, the hydrophobic siloxane segments migrate away from the interface with the ink, and the more hydrophilic segments come into contact with the ink. The interfacial restructuring reduces the interfacial tension, and thus, the tendency for dewetting of the ink, and must take place quite quickly, in a matter of seconds. Silicone copolymers which exhibit a lower rate of interfacial restructuring in contact with water [145,148,152] are not expected to be very writeable with waterbased inks. The requirements stated by Mertens et al. for an acceptable combination of writeability and stability in the release force included a receding water contact angle less than 25° (i.e., a large hysteresis in water contact angle), a difference in the hydrated and dry T_g of the non-silicone matrix being greater than 20°C (i.e., the water needs to plasticize the coating sufficiently to facilitate restructuring), and a hydrated T_g between -15°C and 35°C. Hydrated T_g values less than -15°C tended to result in unstable PSA release forces, while hydrated T_g values greater than 35°C did not provide rapid

may be added to create a surface texture that is more receptive to marking with a pencil or with roller ball pens due to the additional friction that the fillers provide.

Yamamoto and Minamizaki [159] disclose the use of a curable silicone based release agent blended with resin particles which swell or are soluble in organic solvent. Coatings made with such blends can be written on with solvent based inks. For example, an addition cure silicone network containing 20 wt% 0.1 μm diameter PMMA particles exhibited both good writeability (no ink dewetting and smear free) and a low release force of 10 g/cm for a PSA tape.

Several patents discuss the use of alkyl side chain type LABs, blended with various film forming resins, to provide release coatings that can be printed with solvent based flexographic inks [160–162]. For example, Truskolaski and Pohl [162] disclose a blend of polyvinyl *N*-octadecyl carbamate [82] and chlorinated polyolefin resin. They teach that heating the tapes coated with this release blend above the melting point of the polyvinyl *N*-octadecyl carbamate softens the release coating making the resulting printed image adhere better to the tape backing. Blends of a film forming polymer and a silicone containing release material have also been disclosed as release coatings that can be printed with flexographic inks [163].

Several approaches have been disclosed to make release coatings that can be printed with ink jet or laser jet printers (e.g., to make linerless labels). For example, Khatib and Langan [164] disclose a blend of two different acrylate functional silicones, one with a high level of acrylate functionality to provide the printability and one with a low level of acrylate functionality to provide easy PSA release. Lievre and Mirou [165] describe an aqueous blend of a crosslinkable silicone and poly(vinyl alcohol–vinyl acetate) resins while Shipston and Rice describe a blend of acrylic resin and a surfactant [166].

Another example of an application requiring a printable release coating is a linerless roll of postage stamps. The release coating must be able to accept the cancellation inks used by the post office, which are typically glycol based. In order for the cancellation mark to be smear free in a short period of time, the release coating must be able to absorb the ink quickly. One approach that has been disclosed to accomplish this is to blend a silicone containing polyurea, such as those taught in Tushaus and Weiderholt [129], with calcium carbonate and polyvinyl pyrrolidone [167]. Another approach is to blend a condensation or addition curable silicone with polyurethane, polyamide, or polyurea resin particles [168].

As discussed by Yarusso [6], as the rate at which a PSA tape is peeled from a release coated backing increases, a transition from smooth peel to shocky or raspy peel is often encountered. This shocky peel is typically accompanied by an undesirably high noise level, particularly for large jumbos of tape in a factory setting. Therefore, there has been an effort to develop tapes which exhibit quiet and smooth unwind characteristics. Some of the factors which can affect the shockiness include the stiffness and surface topology of the backing, the

rheology of the PSA and release coating, and the level of the release force. Stiffer backings, PSAs, and release coatings tend to promote shocky unwind. Several patents have discussed approaches for reducing the PSA stiffness in order to promote smooth unwind, including the addition of oil to the PSA [169], and the use of styrene-diene block copolymer PSAs having specific levels of diblock and tackifier content, as well as a glass transition temperature within a certain range [170]. Backings with microtopographical features have also been disclosed as a way of reducing shockiness at higher peel rates [171]. The shockiness can also be affected by the choice of the release coating, with stiffer release coatings, such as the crystalline alkyl side chain type polymers, tending to provide more shocky peel. Elastomeric silicone networks with low crosslink density can provide smooth peel, but the peel forces may be too low for the intended application (e.g., tape rolls or liners with modified release level). Higher peel forces can be obtained, for example, with epoxy or acrylate functional silicones having a higher level of epoxy or acrylate functionality; however, this also results in a higher crosslink density and a greater tendency for shocky or raspy release. A blend of two silicones, one having a high level of functionality, and the other having a low level of functionality, has been proposed to obtain simultaneously a modified release level and smooth release for epoxy [172] or acrylate [173] functional silicones. Alternatively, Kessel et al. [174] have proposed using an epoxysilicone having both a low level of epoxy groups, to reduce the crosslink density and shockiness, as well as a high level of alkyl, aryl, or alkyl aryl substitution (e.g., styryl groups), to increase the release force. Lu [175] disclosed the addition of higher alkyl acrylate comonomers (e.g., octyl or decyl acrylate) to a blend of acrylate functional silicones in order to simultaneously increase the release force and maintain smooth peel. The higher alkyl acrylates copolymerize with the silicone acrylates, reducing the crosslink density and forming low T_g acrylate polymer, which help to maintain a low coating modulus. In contrast, the addition of MQ resins as a release modifier led to a stiffer coating promoting raspy or shocky peel.

Another property that can be desired of release materials is 'slippery feel' or low coefficient of friction. This is of particular concern in applications where the liner is smoothed over a part by hand, as when transfer tape is adhered to a substrate. Rubbery feel (high friction) occurs in liners in which the silicone network is highly crosslinked, like the solvent free addition cure, or highly functional radiation cure materials. Related to the discussion above on the modification of raspy peel, the coefficient of friction can be modified by the addition of higher molecular weight, less functional silicones. Lowering the crosslink density of a silicone network will lead to lower friction. In practical application to solvent free silicone systems, only a small amount of high molecular weight material must be added to obtain the slippery feel, and processing viscosity need not be detrimentally effected [51,52].

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D.F. Kinning and H.M. Schneider

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569

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Release coatings for pressure sensitive adhesives

571

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